

# Reactions of 2-phenyl-2,3-dihydro-1,3-phenalenedione anion with haloalkanes and ethyl monohaloacetate

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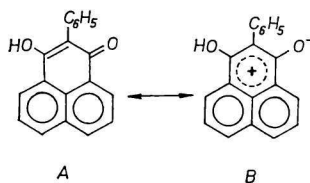
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Reactions of 2-phenyl-2,3-dihydro-1,3-phenalenedione anion with ethyl monohaloacetate and monoalkanes were carried out. It was found that O and C derivatives were formed during these reactions. The C/O ratio depended on the nature of the used solvents (DMFA, DMSO, acetonitrile, acetone, ethanol, butanol). The greatest quantity of C derivative was obtained in DMFA and DMSO. The validity of Kornblum rule was confirmed.

Reaction of 2-phenyl-1,3-indandione with primary haloalkanes give always the thermodynamically more stable C derivatives independently of the solvent and halogen (see [1] and references cited therein).

The different stability of the enol form of 2-phenyl-1,3-indandione and 2-phenyl-2,3-dihydro-1,3-phenalenedione (*I*) as well as the supposed difference in the electron density distribution in the anions of these compounds was the reason for our study of the reactions of the anion *I* with electrophiles.

2-Phenyl-1,3-indandione appears in nonpolar solvents in the diketo form and in polar ones as anion of the enol form [2]. Contrary to that, according to [3] and [4], *I* appeared in chloroform as well as in the solid state only in the enol form though in [5] also ionization was assumed. The stretching vibration of the OH group of *I* appeared at  $3520\text{ cm}^{-1}$  ( $\text{CHCl}_3$ ) and that of the C=O bond at  $1645\text{ cm}^{-1}$ . The relatively low value of the C=O stretching vibration could be attributed to the structure shown by mesomeric formula (Scheme 1). This is in agreement with the structure of analogous compounds, e.g. the

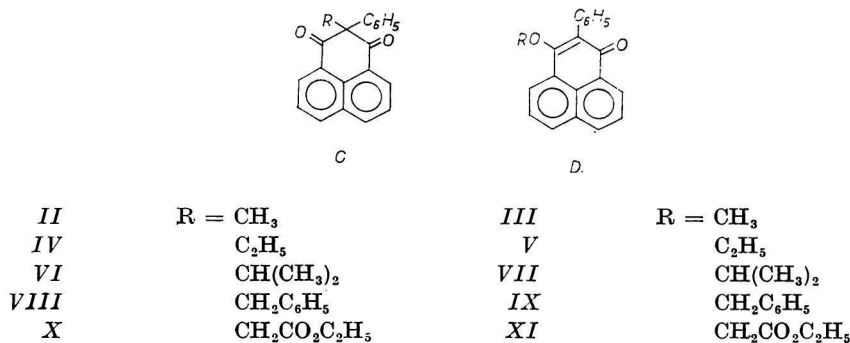


Scheme 1

dipole moment of 1-phenalene is abnormally high [6]. It was possible to presume the activity of the state *B* also on the basis of the high delocalization energy ( $5.827\beta$ ) of the phenalene cation [7]. Knowing the mentioned facts, it was reasonable to believe that the anion *I* would react with electrophiles rather on oxygen than on carbon contrary to 2-phenyl-1,3-indandione anion.

The reactions of the anion *I* with monohalohydrocarbons and ethyl monohaloacetate were carried out in the following solvents: dimethyl sulfoxide (DMSO), dimethylformamide (DMFA), acetonitrile, acetone, ethanol, butanol.

All the reactions, except that with ethyl bromide, showed that the anion *I* reacted with the used electrophiles either on oxygen giving 2-phenyl-3-RO-1-phenalene (structure *C*) or on carbon giving 2-phenyl-2-R-2,3-dihydro-1,3-phenalenedione (structure *D*) (Scheme 2).



Scheme 2

It can be seen from the results in Table 1 that the ratio of C and O derivatives was influenced by the nature of both the solvent and the leaving halogen. The greatest quantity of C derivative was formed in DMSO and DMFA, *i.e.* in solvents with higher dielectric constant. The smallest quantity of C derivative was obtained in acetone, *i.e.* in the

Table 1

Total yield and ratio of C and O derivatives forming in the reaction of 2-phenyl-2,3-dihydro-1,3-phenalenedione anion with halo derivatives in various solvents

Halo derivative	Dimethyl-sulfoxide	Dimethyl-formamide	Aceto-nitrile	Acetone	Ethanol	<i>n</i> -Butanol
ICH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	39.2	28.42	40.8	49.2	42.8	40.5
BrCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0.75	0.838	0.303	0.375	0.095	0.093
	18.2	33.35	19.5	57.6	21.1	21.0
ClCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0.212	0.200	0.093	0.009	0.021	0.025
	13.9	24.38	15.2	43.2	10.5	9.5
ICH <sub>3</sub>	0.187	0.153	0.067	0.004	0.009	0.009
	28.02	64.42	52.4	83.9	13.3	12.9
IC <sub>2</sub> H <sub>5</sub>	2.76	1.256	1.205	1.185	1.029	1.026
	25.3	38.7	38.01	52.6	10.9	10.5
BrC <sub>2</sub> H <sub>5</sub>	0.100	0.074	0.035	0.024	0.022	0.019
	22.9	35.2	34.2	48.9	9.9	9.5
ICH(CH <sub>3</sub> ) <sub>2</sub>	0	0	0	0	0	0
	28.1	31.2	25.6	34.5	15.8	12.6
ICH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.023	0.021	0.021	0.015	0.009	0.008
	42.5	68.2	56.1	65.9	39.2	38.8
BrCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3.801	4.21	1.305	0.674	0.655	0.618
	36.8	59.2	49.2	52.2	26.9	25.6
ClCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1.595	1.55	1.192	0.484	0.504	0.459
	21.1	53.8	26.9	49.5	20.5	19.8
	0.73	0.967	0.286	0.257	0.274	0.251

solvent with the lowest dielectric constant. The C/O ratio in alcohols was low. These results are in accordance with those obtained in reactions of anions of 2-(1-naphthyl)-1,3-indandione, 2-(1-X-2-naphthyl)-1,3-indandione, and 2-(1-X-phenyl)-1,3-indandione with analogous electrophiles in the mentioned solvents [9–12]. The effect of aprotic solvents on the C/O ratio was connected with the ability to solvate cations [13, 14] and perhaps, to a low degree, with the solvation of the ambident anion. Reactions in acetone gave higher percent of O derivatives than in DMSO and DMFA. We attributed this fact to lower solvation ability of acetone in comparison with that of DMSO or DMFA.

It is probable that ambident anions are more solvated on atoms with higher electron density. However, the final result of reactions depended not only on the solvation properties of the anion and cation but above all on the properties of the ambident anion itself. It was demonstrated by different effect of aprotic solvent on the C/O ratio in reactions of acetylacetone and ethyl acetoacetate anions where the greatest quantity of O derivative was obtained in solvents with the highest dielectric constant [15–17], *i.e.* the effect of solvent in these cases was reverse to that found in reactions with cyclic  $\beta$ -diketone anions. However, these differences can result also from geometry of transition states of the ambident anions. While the anion of ethyl acetoacetate can react in both "U" and "W" forms [18], anions of cyclic  $\beta$ -diketones can be active only in the "W" form. Though we were not able to determine the dependence of C/O on the concentration of the reacting components in solvents other than acetone due to the low C/O ratio, it seemed that this ratio would only slightly depend on the concentration of the reacting components in the solvent (Table 2).

Table 2

Yield of C and O derivatives obtained by the A procedure with  $\text{CH}_3\text{I}$  in acetone at various concentrations and temperatures

Acetone [ml]	Reaction temperature [°C]	C Derivative [%]	O Derivative [%]
20	40	54.1	45.9
30	40	55.0	45.0
60	40	56.8	43.2
90	40	55.6	44.4
240	40	57.2	42.8
60	Reflux	48.5	51.5

In agreement with [16, 17, 19], we obtained low yields of O derivatives in alcohols because they solvated well also anions by the centre of the highest electron density under the formation of hydrogen bond.

To verify the validity of Kornblum rule [2, 21] in reactions of the anion I with benzyl halogenides and ethyl monohaloacetate, we used chlorine, bromine, and iodine derivatives. The quantity of O derivative (Table 1) increased in the following order



This order was valid for all aprotic solvents and alcohols. Thus the validity of Kornblum rule was confirmed in all solvents, *i.e.* the increase of positive charge on the electro-

philic centre resulted in increased yields on the more electronegative atom of the ambident anion *I*. When it is expressed in terms of hard and soft acids and bases, which are often used for explanation of reactivity of ambident anions [22–24], the increase in hardness of the electrophilic centre resulted in a greater tendency to react on the harder (*i.e.* more electronegative) atom (symbiotic effect).

Reactions of *I* with diazomethane gave only O-methyl derivative which was in agreement with the mentioned symbiotic effect. The obtained results confirmed the already known fact that stabilization of the enol form increased the ability of the ambident anion of  $\beta$ -diketo compound to react on oxygen. We assume that the difference in the reaction ability of 2-phenyl-1,3-indandione and 2-phenyl-2,3-dihydro-1,3-phenalenedione anions is due to the different electron density distribution and stability of RO derivatives. 2-Phenyl-3-RO-1-phenalenes are more stable than 2-phenyl-3-RO-1-inden-3-ones because they are stabilized by aromatization of the ring (structure *B*) [6, 7] as we have shown it on the starting compound *I*.

The structures of the formed C and O derivatives were confirmed by their infrared and electronic spectra. The obtained C-alkyl derivatives (Table 3) showed two bands of the C=O stretching vibrations at 1660–1670  $\text{cm}^{-1}$  (more intensive) and at 1700–1710  $\text{cm}^{-1}$ . These positions were analogous to those of 2-alkyl-2-aryl-1,3-indandiones [25]. The more intensive band (lower wavenumbers) belonged to asymmetric stretching vibration ( $\nu_{\text{as}}$ ) and the second one (higher wavenumbers) to symmetric stretching vibration ( $\nu_{\text{s}}$ ). The positions of these bands were at lower wavenumbers than those of analogous 2-alkyl-2-phenyl-1,3-indandiones. For example, 2-methyl-2-phenyl-1,3-indandione had  $\nu_{\text{as}}$  at 1713  $\text{cm}^{-1}$  and  $\nu_{\text{s}}$  at 1751  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) [25], while the corresponding values of 2-methyl-2-phenyl-2,3-dihydro-1,3-phenalenedione were 1680 and 1705  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).

Table 3

Analytical data of the prepared compounds

Compound	Formula	<i>M</i>	M.p. [°C] (Kofler)	Calculated/found		$\nu(\text{C}=\text{O})$ [ $\text{cm}^{-1}$ ]	$\nu(\text{C}=\text{C})$ [ $\text{cm}^{-1}$ ]
				% C	% H		
<i>II</i>	$\text{C}_{20}\text{H}_{14}\text{O}_2$	286.2	186–188	83.90	4.89	1680	
				84.20	5.01	1705	
<i>III</i>	$\text{C}_{20}\text{H}_{14}\text{O}_2$	286.2	117–118	83.90	4.89	1650	1630
				83.80	4.93		
<i>IV</i>	$\text{C}_{21}\text{H}_{16}\text{O}_2$	300.2	184–185	84.0	5.34	1675	
				83.92	5.31	1700	
<i>V</i>	$\text{C}_{21}\text{H}_{16}\text{O}_2$	300.2	124–125	84.0	5.34	1640	1625
				83.91	5.47		
<i>VI</i>	$\text{C}_{22}\text{H}_{18}\text{O}_2$	314.2	200–202	84.01	5.73	1675	
				84.00	5.71	1700	
<i>VII</i>	$\text{C}_{22}\text{H}_{18}\text{O}_2$	314.2	130–131	84.01	5.73	1645	1625
				83.75	5.83		
<i>VIII</i>	$\text{C}_{26}\text{H}_{18}\text{O}_2$	362.3	196–197	86.25	4.97	1670	
				86.00	4.98	1695	
<i>IX</i>	$\text{C}_{26}\text{H}_{18}\text{O}_2$	362.3	146–146.5	86.25	4.97	1640	1625
				86.04	4.92		
<i>X</i>	$\text{C}_{23}\text{H}_{18}\text{O}_4$	358.2	189–190	77.1	5.03	1685	
				77.05	5.43	1710	
<i>XI</i>	$\text{C}_{23}\text{H}_{18}\text{O}_4$	258.2	128–129	77.1	5.03	1640	1640
				76.53	5.02		

This shift to lower wavenumbers with derivatives of *I* could be explained by higher polarity of the C=O bond as well as by the fact that  $\beta$ -dicarbonyl system is a part of a six-membered ring.

Compounds obtained by O alkylation had different i.r. spectra in the region of CO vibration. This group of compounds showed only one band of the C=O stretching vibration at 1645–1655  $\text{cm}^{-1}$ , which value was by 55–60  $\text{cm}^{-1}$  lower than that obtained with 1-alkoxy-2-phenyl-1-inden-3-ones. An intensive band belonging to the C=C stretching vibration of the six-membered ring appeared at 1640  $\text{cm}^{-1}$  on the spectra of these compounds. Those C and O derivatives which were formed by reaction with ethyl mono-haloacetate showed another band at 1740–1760  $\text{cm}^{-1}$  belonging to the stretching vibration of the ester carbonyl group.

The prepared C and O derivatives had different electronic spectra. In the molecule of C derivatives both aromatic systems (2,3-dihydrophenalene and benzene) are oriented in-plane because they are connected by  $sp^3$  carbon. In the molecule of O derivatives the phenalene and benzene rings are connected by  $sp^2$  carbon, which enables the plane conformation of these aromatic systems. Therefore all the O derivatives had a long wavelength band (as a result of  $\pi \rightarrow \pi^*$  transition of the whole conjugated system) shifted to higher wavenumbers when compared with those of C derivatives (Fig. 1).

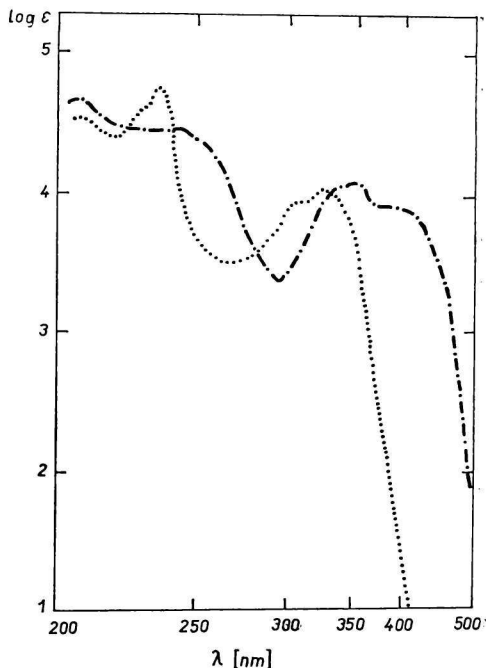
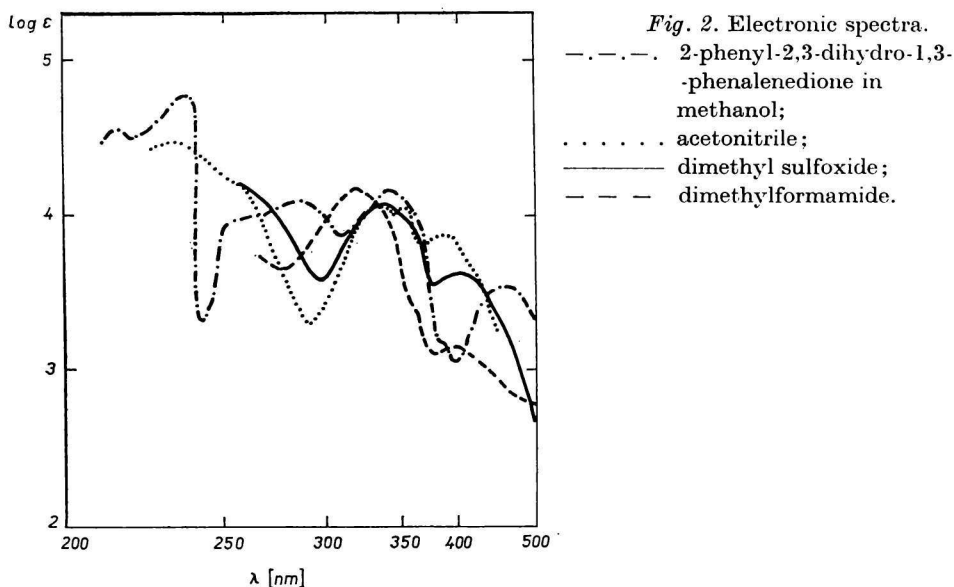


Fig. 1. Electronic spectra.

..... 2-methyl-2-phenyl-2,3-dihydro-1,3-phenalenedione;  
 -.-.-. 2-phenyl-3-methoxy-1-phenalene in methanol.

The electronic spectrum of the initial 2-phenyl-2,3-dihydro-1,3-phenalenedione was more complicated than that of the prepared C and O derivatives and varied rather significantly with various solvents (Fig. 2).



### Experimental

2-Phenyl-2,3-dihydro-1,3-phenalenedione (*I*) was prepared according to [8].

Infrared spectra of the prepared compounds were taken with a double-beam prism UR-20 (Zeiss, Jena) spectrophotometer in the region of 700–2000  $\text{cm}^{-1}$  using NaCl optics. The apparatus was calibrated with a polystyrene foil. The samples were prepared as nujol mulls (the weight ratio of the compound to the nujol was 4 mg/15 mg). The spectrum of nujol was compensated.

Electronic spectra were measured on a Perkin–Elmer, Model 450 spectrophotometer in the 215–750 nm region using  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$  M solutions and cells of 1.00 cm thickness.

#### *Reactions of anion I with halo derivatives*

##### *A. Procedure in DMFA, acetonitrile, acetone, and DMSO*

To the mixture of dried solvent (60 ml), compound *I* (0.005 mole), and anhydrous potassium carbonate (0.015 mole), ethyl monohaloacetate (monohalohydrocarbon; 0.01 mole) (see Table 1) was added after 5 min and the reaction mixture was heated at  $40 \pm 1^\circ\text{C}$  for 8 hrs. Then the solvent was distilled off and the dry residue was boiled twice with benzene (120 ml). The solution was filtered, evaporated to 50 ml, and separated on alumina (Brockmann II, Reanal, Budapest), column ( $2 \times 30$  cm) using benzene as elution agent. The colourless C derivative was eluted first and then the yellow zone containing the O derivative. The unchanged *I* remained on the start. The individual eluates were evaporated to dryness, weighed, and crystallized from ether. The yields are given in Table 1, the analytical data in Table 3.

##### *B. Procedure in ethanol and butanol*

To alcoholate solution prepared from sodium (0.2 g) and dry ethanol (butanol; 60 ml) compound *I* (0.005 mole) and after 5 min the appropriate ethyl haloacetate (halohydro-

carbon; 0.01 mole) were added. Then the reaction mixture was heated at  $40 \pm 1^\circ\text{C}$  for 8 hrs. The further procedure was the same as in *A*.

### 2-Phenyl-3-methoxy-1-phenalenone (III)

Diazomethane (0.01 mole) dissolved in diethyl ether (30 ml) was added to *I* (0.005 mole) in diethyl ether (30 ml). The reaction mixture was allowed to stay at room temperature for 5 hrs. The further procedure was the same as in *A*. Yield 45%.

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